

electrochemical process in Equation 1:

F is the Faraday number; and

PH_2 is the partial pressure of hydrogen at the interface between the ceramic and the platinum layer coated onto it.

Elimination of the square root function, conversion to common logarithms, and substitution of the accepted values for R, T, n and F gives:

$$E = k + 0.02957 \log(PH_2) \text{ volts}$$

in which 0.02957V is the Nernstian slope of the equation at 25° C. A plot of device output voltage against the logarithm of the hydrogen partial pressure yields a calibration curve for the device. A calibration curve for the device described above was obtained by measuring the device emf at about 25° C. when exposed to varying concentrations of hydrogen in nitrogen. The resulting calibration curve is shown in FIG. 2: the data is very close to the expected slope for this curve. It is noted that this calibration curve covers a wide range of hydrogen gas concentrations, from 0.01% up to 100%.

In U.S. Pat. No. 5,453,172 Alberti et al. indicate that there are drawbacks with using a silver electrode in contact with zirconium hydrogen phosphate which can lead to a total reduction of Ag^+ in such a system. Although the Nazirpsio ceramic used in this device is a complex phosphate bonded sodium hydronium zirconium silicophosphate, no difficulties of this nature have been encountered with the silver electrode used in conjunction with the silver ion containing modified layer in the ceramic in this device. It has also been found that if a silver electrode, for example the silver containing cement described above, is used without a silver ion containing modified layer in the surface of the Nazirpsio ceramic, a satisfactory reference electrode is not obtained and the device does not provide reliable or reproducible results.

For a hydrogen sensor to be useful, it is desirable that it react reasonably quickly to a change in hydrogen concentration. FIG. 3 demonstrates the speed with which the device described above responds to various concentrations of hydrogen in nitrogen, after the device had been exposed to air. For concentrations above about 1% the response time is of the order of 5 seconds or less to obtain a signal corresponding to about 90% of the final steady state value. At lower concentrations the response time increases. FIG. 4 demonstrates the speed with which the device described above responds to changes of hydrogen concentration without exposure to air in between the changes in hydrogen concentration. Again at concentrations above about 1% the response time is very short and is of the order of a few seconds and at lower concentrations the response time is somewhat longer.

It can thus be seen that this invention provides a simple and rugged hydrogen detection and measuring device. The device is capable of operating in contact with hydrogen concentrations or partial pressures ranging upwardly from quite low values to effectively 100%. Further, the device does not require an independent pure hydrogen gas supply for its reference electrode.

We claim:

1. A hydrogen detection device comprising in combination:

- (a) a body of phosphate bonded ceramic electrolyte of the general formula $Na(H_3O)_xZr_2Si_xP_{(3-x)}O_{12}$ having a first face spaced apart from a second face;
- (b) a layer of platinum on the first face of the body in electrical contact with the ceramic electrolyte;

(c) a silver ion modified layer on and in the second face of the body;

(d) a silver electrode in contact with the silver modified layer; and

(e) conductive leads electrically connected to each of the faces;

whereby the emf generated when the ceramic body is exposed to hydrogen gas is measured.

2. A hydrogen detection device according to claim 1 wherein the first and second spaced apart faces on the ceramic body are substantially parallel to each other.

3. A hydrogen detection device according to claim 1 wherein the first and second faces are each substantially flat.

4. A hydrogen detection device according to claim 1 wherein the first and second spaced apart faces on the ceramic body are substantially parallel to each other, and wherein the first and second faces are each substantially flat.

5. A hydrogen detection device according to claim 4 wherein the ceramic body is disc shaped, and the first and second faces comprise the two faces of the disc.

6. A hydrogen detection device according to claim 1 wherein the silver electrode comprises a silver containing conductive cement applied over the silver ion modified layer.

7. A hydrogen detection device according to claim 1 wherein the two conductive leads are attached to each of the platinum layer and the silver electrode by means of a conductive cement.

8. A hydrogen detection device according to claim 1 wherein the same silver containing conducting cement is used as both the silver electrode and to attach the two conductive leads.

9. A hydrogen detection device according to claim 1 wherein the two conductive leads are both silver.

10. A hydrogen detection device according to claim 1 wherein in the body of ceramic electrolyte of the general formula $Na(H_3O)_xZr_2Si_xP_{(3-x)}O_{12}$, x has a value of from about 1.3 to about 2.2.

11. A hydrogen detection device according to claim 10 wherein x has a value of about 1.5.

12. A method of detecting hydrogen in a gaseous system which comprises exposing a detection device comprising in combination:

(a) a body of phosphate bonded ceramic electrolyte of the general formula $Na(H_3O)_xZr_2Si_xP_{(3-x)}O_{12}$ having a first face spaced apart from a second face;

(b) a layer of platinum on the first face of the body in electrical contact with the ceramic electrolyte;

(c) a silver ion modified layer on and in the second face of the body;

(d) a silver electrode in contact with the silver ion modified layer; and

(e) conductive leads electrically connected to each of the faces;

to the gaseous system, and measuring the emf generated across the two conductive leads.

13. A method of measuring the concentration of hydrogen in a gaseous system which comprises:

(i) exposing a detection device comprising in combination:

(a) a body of ceramic electrolyte of the general formula $Na_{(1+x)}Zr_2Si_xP_{(3-x)}O_{12}$ having a first face spaced apart from a second face;

(b) a layer of platinum on the first face of the body in electrical contact with the ceramic electrolyte;

(c) a silver ion modified layer on and in the second face of the body;

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(d) a silver electrode in contact with the silver ion modified layer; and

(e) conductive leads electrically connected to each of the faces;

to a plurality of gaseous systems each containing known amounts of hydrogen;

(ii) measuring the emf generated across the conductive leads by exposure to each gaseous system to provide a calibration curve for the device;

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(iii) exposing the device to a gaseous system containing an unknown amount of hydrogen;

(iv) measuring the emf generated on exposure to gaseous system in step (iii); and

(v) comparing the emf measured in step (iv) with the calibration curve obtained in step (ii).

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